

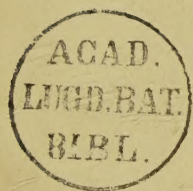
TUNGSTATES AND MOLYBDATES

OF

THE RARE EARTHS.

Thesis

Presented to the Department of Philosophy of the
University of Pennsylvania,
For the Degree of Doctor of Philosophy.



BY

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The Tungstates and Molybdates of the Rare Earths.

The estimation of molybdic and tungstic acids, and their separation from each other have been the subject of many investigations, but notwithstanding the time and care expended the results so far attained are not perfectly satisfactory, particularly as regards their separation. The reactions which take place when either element is tested alone cannot be depended upon when the two are together, each seeming to exert some modifying action on the other.

Some years ago, Smith and Bradbury* carried out a long series of experiments on the precipitation of these two acids, chiefly with salts of the heavy metals. Their research brought out many new and interesting facts relating to the precipitation and estimation of each acid separately, but failed to produce anything new in the way of a separation. It was with the hope that, by extending the investigation begun by them, to the action of other precipitants on these acids, additional information might be gathered which would lead to more definite results, that the experiments were undertaken, the results of which are offered in the following pages.

The work was commenced at the suggestion of Dr. Edgar F. Smith, and carried out in his laboratory, and I avail myself of this opportunity to acknowledge his constant interest in the work, and to thank him for the unfailing kindness which rendered it possible for me to carry it out. The work has occupied nearly two years. Many difficulties have been encountered, and although the results obtained are

* *Journal of Analytical and Applied Chemistry*, September, 1891.

not of the nature expected, yet I hope they may prove of some value as an addition to our knowledge of the behavior of molybdic and tungstic acids with other elements.

The molybdate solutions used in the work were made up from the sodium molybdate, crystallizing with two molecules of water, and prepared by E. Merck, Darmstadt. Analysis showed the salt to be pure and to agree with the formula given, $\text{Na}_2 \text{MoO}_4 + 2 \text{H}_2\text{O}$.

The tungstate solutions were prepared from the corresponding tungsten salt, $\text{Na}_2 \text{WO}_4 + 2 \text{H}_2\text{O}$. The salt used was made by H. Trommsdorf, Erfurt, and analysis showed that traces of silica and ferric iron were present, and molybdic trioxide was found to the amount of three and one-tenth per cent. This was separated by Pechard's method.* The sodium tungstate was fused, and powdered; one gram of this material in a porcelain boat was heated in a current of dry hydrogen chloride gas at a temperature of 250°C . until no more $\text{MoO}_3 + 2 \text{HCl}$ formed. The hydrogen chloride gas after passing over the boat was conducted into distilled water acidulated with nitric acid. When the operation was over the tube containing the boat was allowed to cool before the current of gas was discontinued. The boat was removed, and the contents of the tube dissolved out with ammonia, and the tube thoroughly washed with distilled water. The ammoniacal solution with the washings from the tube, as well as the water through which the hydrogen chloride gas had been conducted, were evaporated to dryness, in a porcelain crucible, ignited gently to expel all ammonium salts, and the molybdic trioxide weighed as such.

On examining the contents of the boat it was found that a hard crust had formed on the top; the mass was therefore removed and powdered very fine, after which it was again heated in a current of hydrogen chloride gas, when more

* *Comptes rendus*, 114, p. 173.

molybdenum trioxide was obtained. The process was repeated six times, after which no more molybdic trioxide was obtained.

Due allowance has been made in all calculations for the amount of molybdic acid found in the sodium tungstate.

It was found best not to prepare more than 250 cc. of the solution of sodium tungstate at one time, as on standing it gradually affects the flask, the glass being attacked, and a sediment appearing which resembles silica, and is of noticeable amount. The solution of sodium molybdate also attacked the glass, but not so strongly nor so quickly as the sodium tungstate.

The atomic mass of molybdenum is taken as 96, and that of tungsten as 184 in the calculations of the different salts obtained.

Sodium Tungstate and Manganese Sulphate.

Atomic mass of manganese = 55.

The solution of manganese sulphate used was a saturated one. The solution of sodium tungstate contained 27.8600 grammes to the litre, and, if completely precipitated by the manganese sulphate, 10 cc. of the solution should yield 0.2871 grammes of manganese tungstate, Mn WO_4 .

The precipitates all showed the same character however varied the conditions under which they were formed, being flocculent at first; and becoming slimy on standing. They filtered very slowly and were difficult to wash.

The filtrations were made through asbestos in a Gooch crucible, and the filtrates were all tested for tungstic acid by hydrogen sulphide in ammoniacal solution, the solution being subsequently acidified with hydrochloric acid.

A. Exp. 1. Ten cc. of the sodium tungstate solution were diluted to 250 cc. with distilled water, brought to boiling, and 50 cc. of the manganese sulphate solution added. A voluminous precipitate formed at once, which was allowed to settle, then filtered off, washed with boiling water, dried in an air bath at 180°C ., cooled in a desiccator for three hours and weighed.

Wt. obtained.	Wt. calculated.	Difference.
0.2310 gram.	0.2871.	—0.0561 gram.

The filtrate gave a precipitate of tungsten trisulphide.

Exp. 2. Ten cc. of the sodium tungstate solution were treated as before, but the precipitate was allowed to stand for two days, then filtered cold, and washed with hot water.

Wt. obtained.	Calculated.	Difference.
0.2779 gram.	0.2871.	—0.0092.

The filtrate gave a precipitate of tungstic trisulphide.

Exp. 3. Ten cc. sodium tungstate solution were treated as before; the precipitate allowed to stand for twelve hours, then filtered cold and washed with cold water.

Wt. obtained.	Calculated.	Difference.
0.2667 gram.	0.2871.	—0.0204.

Exp. 4. Ten cc. sodium tungstate solution were treated as before; the precipitate was allowed to stand for twelve hours, then brought to boiling, filtered hot, and washed with a hot solution of ammonium nitrate.

Wt. obtained.	Calculated.	Difference.
0.2110 gram.	0.2871.	—0.0693.

B. Exp. 1. Ten cc. sodium tungstate solution were diluted to 250 cc. with distilled water, and five grammes of ammonium nitrate added; the whole was then brought to boiling, and 50 cc. of the manganese sulphate solution

were added; the precipitate was allowed to subside, filtered off, and washed with water containing ammonium nitrate; the filtrate was perfectly clear.

Wt. obtained.	Calculated.	Difference.
0.2351 grm.	0.2871.	—0.0520.

Exp. 2. Ten cc. sodium tungstate solution were treated as in *B 1*. The precipitate was allowed to stand over night before filtering, was filtered cold, and washed with cold water containing ammonium nitrate.

Wt. obtained.	Calculated.	Difference.
0.2393 grm.	0.2871.	—0.0478.

Both filtrates gave tungsten trisulphide.

C. Exp. 1. Ten cc. sodium tungstate solution were diluted to 250 cc. with distilled water, and 80 cc. of 95 per cent alcohol were added; then 50 cc. manganese sulphate solution. The solution was heated, and the precipitate formed slowly. It was voluminous, white and flocculent, becoming granular on standing; it was filtered off while still hot, washed with 33 per cent alcohol, and ignited at a low temperature.

Wt. obtained.	Calculated.	Difference.
0.2707 grm.	0.2871.	—0.0164.

Exp. 2. Ten cc. sodium tungstate solution were treated as in *C 1*. The precipitate was allowed to stand for several days before filtering, was filtered cold, and washed with 33 per cent alcohol as before.

Wt. obtained.	Calculated.	Difference.
0.2666 grm.	0.2871.	—0.0205.

A brief inspection of the analytical results given in detail above shows beyond reasonable doubt that the precipitation of tungstic acid from its salts cannot be well hoped for when manganese salts are used as the precipitants. The most varying conditions failing to give any promise of even

approximate success, further experiments with manganese salts were abandoned, and attention was turned to uranium salts. Trials were made with uranium acetate, uranyl nitrate and uranyl chloride. With uranium acetate no precipitate formed in an aqueous solution of sodium tungstate, whether cold or hot, and an excess of either the tungstate or the acetate produced no effect. The addition of a few drops of acetic acid caused no change. Alcohol produced a slight opalescence, but though the solution stood for several days no precipitate formed. When uranyl nitrate was used a precipitate formed at once, which was pale yellow in color, flocculent and quick to subside. The precipitation seemed to take place equally well in the presence of alcohol, and in that of ammonium salts.

The solution of sodium tungstate used contained 5 grammes in a litre, and 10 cc. would therefore yield $0.0883 +$ grammes of uranyl tungstate, if completely precipitated. The atomic mass of uranium was taken as 239.6.

A. Twenty cc. sodium tungstate solution were diluted with 20 cc. of distilled water and 5 cc. of a solution of uranyl nitrate added, the latter being in slight excess. This was followed by 25 cc. of a saturated solution of ammonium chloride, and the whole heated to nearly boiling for two hours, after which the precipitate was filtered off and washed first with water containing ammonium chloride, then with pure water. The filtration was made through Schleicher & Schull's 590 filter paper, and the precipitate was ignited strongly with free access of air.

Wt. obtained.	Calculated.	Difference.
0.1728 grm.	0.1767.	0.0039.

The filtrate gave no trace of tungsten trisulphide when tested with hydrogen sulphide, and from the appearance of the precipitate after ignition some reduction had evidently taken place.

B. Twenty cc. sodium tungstate solution diluted with 25 cc. distilled water, were precipitated with 5 cc. of the uranyl nitrate solution. The precipitate was allowed to stand for one hour, was then filtered in the cold, and washed with cold water, on a tared filter which had been dried at 150° C. The precipitate was dried at the same temperature in an air bath for two hours, and weighed at constant weight.

Wt. obtained.	Calculated.	Difference.
0.1770 grm.	0.1767.	+0.0003.

The filtrate when tested gave no trace of tungsten trisulphide. It may be added that when the ammonium chloride used in the first experiment was replaced by alcohol, the precipitation seemed to be equally complete, as there was no evidence of the presence of tungsten when the filtrate was tested with hydrogen sulphide.

To ascertain whether the tungstic acid could be determined volumetrically the following experiment was made:

A solution was prepared containing 14 grams of uranyl nitrate in one litre of water. Twenty cc. sodium tungstate solution were diluted with 25 cc. distilled water, and the uranyl nitrate solution introduced from a burette, the tungstate solution being constantly stirred, and the end reaction ascertained by testing with potassium ferrocyanide on a porcelain plate.

Toward the last the reaction is rather slow, so that a brown color may be obtained with the potassium ferrocyanide before the tungsten is fully precipitated. If, however, the solution is allowed to stand a few seconds after each addition of the uranyl nitrate solution, no coloration is obtained on testing, unless the reaction is complete. By a little care the end reaction can be made extremely close. Upon substituting a solution of uranyl chloride for the nitrate, equally good results were obtained.

Sodium Molybdate and Uranium Salts.

Inasmuch as the precipitation of tungstic acid by manganese salts had proven so unsatisfactory, I did not consider it advisable to experiment with molybdic acid in this direction, but began at once an examination of the behavior of uranium salts with molybdates.

A solution was prepared containing 8.51 grammes of sodium molybdate to the litre, and the same salts of uranium were tried that had been used in the experiments with tungstic acid.

With uranium acetate, sodium molybdate behaved similarly to sodium tungstate, no precipitate being obtained by any method tried. With the nitrate of uranium, however, a precipitate is formed at once which redissolves on stirring, though not completely, a small quantity of some flocculent material remaining undissolved; boiling did not bring down any further precipitate, and an excess of the nitrate had no effect. The uranyl nitrate solution was the same as that used with sodium tungstate, and contained 14 grams to the litre. On trying a concentrated solution of uranyl nitrate a dense precipitate formed at once, which on dilution dissolved in part, but very imperfectly.

Addition of alcohol does not change the behavior in either a cold or a hot solution.

A solution containing 25 cc. of a saturated solution of ammonium chloride, 20 cc. of the sodium molybdate solution, and 25 cc. of water gave no permanent precipitate with uranyl nitrate, but when 20 cc. of the sodium molybdate solution were diluted with 25 cc. water, and the uranyl nitrate solution added in excess, the addition of ammonium chloride brought down the whole of the molybdenum.

With uranyl chloride, a precipitate was obtained at once, which, like that produced by uranyl nitrate redissolved on stirring, as fast as it formed.

On standing, a pale lemon yellow precipitate appeared, which on heating went into solution. With the addition of an excess of uranyl chloride to the cold solution, a precipitate forms similar in appearance to the one just described, but on heating it does not redissolve. Heated for an hour it grows denser, and gradually becomes crystalline. These crystals are insoluble in water, and those which I obtained were washed first by decantation, then on the filter with cold water, dried in the air bath at 128° C. (without any alteration in appearance), and analyzed.

The molybdic acid was determined by the method already described, heating in a current of hydrogen chloride gas. It came off readily at a low heat, the salt in the boat changing in color from a brilliant golden yellow to a light green, then to a golden brown, and finally to a dark green, almost to a black.

This blackish residue when treated with concentrated hydrochloric acid did not dissolve; with aqua regia it did slowly dissolve to a deep yellow solution from which the uranium was precipitated by ammonium hydrate; the precipitate after strong ignition had a metallic appearance. It was dissolved in concentrated nitric acid, evaporated to dryness, and gradually heated to a dull red heat. The brownish yellow powder obtained, was weighed as uranium trioxide.

A slight loss occurred when the salt was heated in the stream of hydrogen chloride gas, as a little was carried over mechanically, and adhered so strongly to the walls of the tube that it could not be removed.

The weight of material taken for analysis was one-tenth of a gramme. The weights obtained were as follows:

$$\text{MoO}_3 = 0.0333 \text{ gramme} = 33.3 \%,$$

$$\text{Ur O}_3 = 0.0620 \text{ gramme} = 62.0 \%.$$

These values correspond very closely to the formula $\text{UrO}_2 \cdot \text{MoO}_4$, when the radicle MoO_4 may be regarded as replacing the two chlorine atoms in the uranyl chloride. The theoretical amounts required for this formula are .

MoO_3 0.0334 gramme = 33.4 %,

UrO_3 0.0666 gramme = 66.6 %.

Water of crystallization does not seem to be present ; one-tenth of a gramme of the substance was dried over sulphuric acid for two days, and then in the air bath for two hours at a temperature of 128°C .; the loss in weight was eight-tenths of a milligramme. On strong ignition the color changed at first to a light green, then to a golden brown, and on cooling became once more bright yellow. By this ignition a loss in weight occurred amounting to nine and three-tenths milligrammes ; a second ignition caused no further loss.

Both before and after ignition the salt is readily soluble in hydrochloric acid, apparently without decomposition, as no reaction for uranium is given by the solution when tested with potassium ferrocyanide.

The perfect precipitation of tungstic acid by uranyl nitrate from the sodium tungstate solution, and the non-precipitation of molybdic acid by the same reagent, encouraged a hope that a separation of the two acids might be possible through its means.

As potassium ferrocyanide indicated the end reaction so sharply between sodium tungstate and uranyl nitrate, some tests were made with it as an indicator, with solutions of sodium molybdate and uranyl nitrate. Observing the same precautions as before the end reaction was equally sharp. It was observed, however, that the red color imparted to the potassium ferrocyanide by a drop of the molybdate solution as soon as the uranyl nitrate was in excess, gradually

disappeared, and was not restored by the further addition of uranyl salts. The conditions were next varied by introducing the potassium ferrocyanide into the molybdate solution instead of making the tests on a porcelain plate as heretofore. Twenty cc. of sodium molybdate were diluted with 25 cc. of water, and 5 cc. of potassium ferrocyanide added. The uranyl nitrate solution was then run in, the red color appearing when $33\frac{1}{10}$ cc. of the uranyl nitrate had been used; an excess of 6 or 7 cc. were added, and a deep red solution formed, but no precipitate appeared. After standing for two hours the red color had disappeared, and the solution had become yellow. A portion of this was tested with potassium ferrocyanide, but no reaction was obtained for uranium.

The addition of uranyl nitrate to another portion showed no excess of the potassium ferrocyanide. On substituting uranyl chloride for the nitrate the red solution was not obtained, but a reddish brown precipitate came down which was much lighter in color than that given by the uranyl salts alone.

Twenty cc. sodium tungstate solution were mixed with 5 cc. of the sodium molybdate solution, and diluted with 25 cc. of water; the uranyl nitrate solution was next run in from a burette, and the end reaction ascertained by potassium ferrocyanide on a porcelain plate. After standing for an hour the precipitate was filtered off in the cold, and washed with 33 per cent alcohol.

It was hoped that the filtrate would contain the molybdenum, but examination showed that the greater part of it had been precipitated with the tungsten.

A second solution was prepared and titrated in the same manner as before; the precipitate with the supernatant fluid was then heated for an hour at a temperature of 60° C. filtered while hot, and washed with hot water containing

33 per cent of alcohol. The molybdic acid was found in both filtrate and precipitate, though more went into the filtrate than in the first case.

On substituting uranyl chloride for the nitrate and repeating the titration, only a slight precipitate of the tungsten formed, the greater part dissolving with the molybdate, as fast as formed.

An excess of uranyl chloride brought down both the tungsten and the molybdenum completely. It was evident that no separation could be hoped for by means of uranium salts. There seems to be a tendency on the part of the members of the chromium sub-group to form compounds with each other which are not readily broken up, and which probably contain complex radicles of as yet unknown constitution. This is very strongly indicated by the behavior of molybdic acid with uranyl salts, and the failure of the resulting compound to react in solution, for uranium with potassium ferrocyanide.

The subject is a very interesting one, and I greatly regret that time did not allow me to follow further the line of research there opened. Investigation in this direction would probably show that molybdic and tungstic acid unite to form stable complex compounds, and that the difficulty with which these are broken up may readily account for the trouble experienced in separating these two elements by the methods ordinarily employed.

As the chief object of my investigations was to ascertain the manner in which the rare earths would act with tungstates and molybdates, these were now taken up and studied in detail. As the quantity at my disposal of any one of the rare earths used was necessarily very limited the material had to be worked over frequently, and a great deal of time was in consequence consumed by this preparatory work.

The following salts were used :

Cerium sulphate.
Praseodymium chloride.
Neodymium chloride.
Lanthanum chloride.
Thorium chloride.
Potassium zirconium fluoride.
Zirconium fluoride.

Sodium Molybdate and Cerium Sulphate.

Atomic mass of cerium = 140.2.

The solution of sodium molybdate used contained 13.24 grammes to the litre, so that 10 cc. of the solution should give 0.1628 gramme of cerium molybdate, $\text{Ce}_2(\text{MoO}_4)_3$ if fully precipitated. The solution of cerium sulphate used was saturated.

Exp. 1. Five cc. of the sodium molybdate solution were diluted to 150 cc. with distilled water, and 10 cc. of the cerium sulphate solution added in the cold. A voluminous, white gelatinous precipitate formed at once. This stood for eighteen hours, when it had become granular in appearance and was yellow in color. It was filtered cold, washed with cold water, ignited and weighed. The theoretical weights are all calculated for the formula $\text{Ce}_2(\text{MoO}_4)_3$.

Wt. obtained.	Calculated.	Difference.
0.0760 grm.	0.0814.	—0.0054.

Exp. 2. Five cc. of the sodium molybdate solution diluted to 150 cc. with distilled water were brought to boiling, when 10 cc. of the cerium sulphate solution were added. A white precipitate formed at once, soon becoming curdy, and then granular, the color changing to yellow. This was

allowed to stand for twelve hours, was then filtered, and washed with hot water, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.0752 grm.	0.0814.	—0.0062.

Exp. 3. Ten cc. sodium molybdate solution were diluted to 300 cc. with distilled water, and 15 cc. of the cerium sulphate solution added in the cold. The precipitate after standing for twelve hours was filtered on asbestos in a Gooch crucible, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.1596 grm.	0.1629.	—0.0033.

Exp. 4. This was a duplicate of No. 3, excepting that the filtration took place as soon as the precipitate had settled.

Wt. obtained.	Calculated.	Difference.
0.1555 grm.	0.1629.	—0.0074.

From both filtrates additional precipitates were obtained on boiling.

Exps. 5 and 6. Ten cc. of the sodium molybdate solution were diluted to 110 cc. with distilled water and brought to boiling, when 15 cc. of the cerium sulphate solution were added; after two hours the precipitate was filtered off, washed with hot water, ignited and weighed.

	Wt. obtained.	Calculated.	Difference.
5.	0.1496 grm.	0.1629.	—0.0133.
6.	0.1587 "	0.1629.	—0.0042.

Exp. 7. Ten cc. Na_2MoO_4 solution were diluted to 110 cc. with distilled water, 15 cc. of cerium sulphate solution added in the cold, and the whole brought to boiling, when 25 cc. of 95 per cent alcohol were added. The precipitate was filtered off through S. S. 590 filter paper, washed with 50 per cent alcohol, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.1588 grm.	0.1629.	—0.0041.

Exp. 8. Ten cc. of sodium molybdate solution were diluted to 110 cc., 15 cc. of cerium sulphate solution added in the cold, the whole brought to boiling, when one-third the volume of 95 per cent alcohol was added. The precipitate stood for twelve hours before filtering; it was apparently not homogeneous, as a fine white powder was mixed through the yellow cerium molybdate. The filtering was very slow, and the washing with 50 per cent alcohol was continued for two days.

Wt. obtained	Calculated.	Difference.
0.2118 grm.	0.1629.	+0.0489.

Exp. 9. Ten cc. sodium molybdate solution were diluted to 100 cc. and 15 cc. cerium sulphate solution added in the cold, followed by one-third the volume of 95 per cent alcohol. The precipitate was filtered after standing for two hours, and like that in No. 8, was not homogeneous in appearance.

Wt. obtained.	Calculated.	Difference.
0.1919 grm.	0.1629.	0.0290.

Exp. 10. Ten cc. of sodium molybdate solution were diluted to 100 cc., and 15 cc. cerium sulphate solution added. The whole was boiled for an hour, allowed to cool, when one-third the volume of 95 per cent alcohol was added. After standing twelve hours, it was filtered, washed with 50 per cent alcohol, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.2126 grm.	0.1629.	0.0497.

The precipitates from 8, 9 and 10, after ignition, were dissolved in hydrochloric acid, and tested with barium chloride; all gave precipitates of barium sulphate, as was expected. The following experiments were then made to determine what proportion of alcohol could be added without causing the cerium sulphate to precipitate.

a. Five cc. of the cerium sulphate solution were diluted to 60 cc., then 20 cc. of 95 per cent alcohol were added in the cold, and, no precipitate forming, more alcohol was added, 5 cc. at a time, until 70 cc. in all had been introduced. The solution still remained perfectly clear.

b. Five cc. of the cerium sulphate solution were diluted to 60 cc., and brought to boiling, when alcohol was added 5 cc. at a time, until 65 cc. had gone in, but the solution still remained clear. To this hot solution the cerium sulphate solution was added in the same way as the alcohol had been. The first addition of 5 cc. caused a precipitate to form, which redissolved at once. The second edition of 5 cc. caused a precipitate which dissolved again very slowly, and with the third addition the cerium sulphate came down in fine needles.

It was evident that the amount of alcohol which had been used in experiments 8, 9 and 10, with the sodium molybdate, had not been sufficiently great to cause by itself the precipitation of the cerium sulphate. The experiments were, therefore, repeated, the conditions being slightly varied.

Exp. 11. Ten cc. sodium molybdate solution were diluted to 100 cc., and 15 cc. of the cerium sulphate solution added. To this, in the cold, 50 cc. of 95 per cent alcohol were added very gradually, and with constant stirring. The whole was allowed to stand for half an hour, when the precipitate was filtered off, washed, first with 50 per cent alcohol then with 30 per cent, and finally with pure water, ignited and weighed. The results obtained were the best of all the series.

Wt. obtained.	Calculated.	Difference.
0.1620 grm.	0.1629.	— 0.0009.

The ignited precipitate dissolved in hydrochloric acid gave no trace of sulphuric acid when tested with barium chloride.

Exp. 12. This was a duplicate of No. 11, except that the final washing was done with 20 per cent alcohol instead of pure water. The washing was continued until there was no reaction with barium chloride for sulphuric acid.

Wt. obtained.	Calculated.	Difference.
0.1799 grm.	0.1629.	+ 0.0170.

The precipitate was tested as before, and proved to contain cerium sulphate.

Exp. 13. Ten cc. of sodium molybdate solution were diluted to 185 cc. and 50 cc. of 95 per cent alcohol added, followed by 15 cc. of cerium sulphate solution. After standing an hour the precipitate was filtered off, and washed in the same manner as in No. 12.

Wt. obtained.	Calculated.	Difference.
0.1644 grm.	0.1629.	0.0015.

From the precipitate barium sulphate equivalent to 0.00146 gramme of cerium sulphate was obtained, and the filtrate gave 0.0007 gramme of molybdenum trisulphide.

Exp. 14. This was a duplicate of No. 13.

Wt. obtained.	Calculated.	Difference.
0.1708 grm.	0.1629.	0.0079.

The precipitate yielded the equivalent of 0.0090 gramme of cerium sulphate with barium chloride.

With hydrogen sulphide a precipitate of molybdenum trisulphide was given by all the filtrates from the experiments described above, the amount varying in wide limits. While alcohol diminished the solubility of the cerium molybdate formed, the advantage gained was more than counterbalanced by the tendency of the molybdate to carry down with it cerium sulphate, in the presence of alcohol.

Sodium Tungstate and Cerium Sulphate.

The solution of sodium tungstate used contained 27.07 grammes in one litre. But few experiments were made, the results obtained being similar to those with sodium molybdate. Precipitation in a water solution alone was very incomplete, the precipitate persistently running through the filter, so that no definite results could be obtained in this way. When alcohol was used better results were obtained, the filtrate coming through clear.

Exp. 1. Ten cc. sodium tungstate solution were diluted to 100 cc. with distilled water, and 25 cc. of 95 per cent alcohol added. The whole was brought to boiling when 25 cc. cerium sulphate solution were added. A dense, flocculent yellow-white precipitate came down at once, subsiding rapidly; it was filtered and washed with 25 per cent alcohol.

Wt. obtained.	Calculated.	Difference.
0.3266 grm.	0.3144.	0.0122.

Exp. 2. Ten cc. of sodium tungstate solution were diluted with distilled water to 100 cc. and 25 cc. of 95 per cent alcohol added, followed by 25 cc. of cerium sulphate solution in the cold. A bluish white precipitate formed, which on standing acquired a yellow tint. This was filtered cold and washed with 25 per cent alcohol.

Wt. obtained.	Calculated.	Difference.
0.3125 grm.	0.3144.	—0.0019.

Exp. 3. Ten cc. of sodium tungstate solution were diluted to 100 cc. and 25 cc. of 95 per cent alcohol added. The whole was brought to boiling and 25 cc. cerium sulphate added. The precipitate was washed with hot 25 per cent alcohol.

Wt. obtained.	Calculated.	Difference.
0.3322 grm.	0.3144.	0.0178.

The precipitate from all three solutions contained cerium sulphate, and the filtrates all showed traces of tungsten.

The next salts taken up were the two very rare ones, neodymium chloride and praseodymium chloride. For the material used I am indebted to the courtesy of Professor Waldron Shapleigh, of the Welsbach Light Company, Gloucester, N. J. The material given me consisted of the oxides prepared from the oxalates by ignition. These oxides are considered by v. Welsbach* (who separated didymium into the two elements neodymium and praseodymium) to be the peroxides, and the formulæ Nd_4O_7 and Pr_4O_7 have been assigned to them.

Nd_4O_7 is a light brown powder, while Pr_4O_7 is dark brown, almost black. Both dissolve readily in hydrochloric acid with evolution of chlorine, and form sesquichlorides. Neodymium chloride, Nd_2Cl_6 , forms a rose colored solution, while the corresponding praseodymium salt is pale green in color. The solutions used were prepared by evaporating the chlorides prepared from the oxides to dryness, taking up with water and again evaporating until all the hydrochloric acid was expelled. The residue was dissolved in water and filtered off from a little insoluble material which was probably a basic salt. About half a gramme of the oxide was taken, and from it 100 cc. of the chloride solution was prepared.

The tungstates obtained from these salts by precipitation with sodium tungstate were gelatinous, and very difficult to filter and wash, showing a strong tendency to pass through the pores of the filter paper.

For this reason a double filter was always used, and even with this precaution it was necessary to use as little pressure as possible with the filter pump, and yet secure filtration. Even with the filter pump the washing was very slow, and generally consumed a day at least, sometimes longer, although the quantities of material used were very small.

* *Wien. Monatsheft*, 6. 477. 1885.

The best results were obtained by washing first by decantation, and then on the filter.

The molybdates are gelatinous when first precipitated, but on heating they gradually become granular, and are then easily filtered and washed.

The neodymium tungstate has a very pale rose tint before ignition, which changes to a lavender color after ignition. The praseodymium tungstate has a decided greenish yellow tint both before and after ignition. The colors of the molybdates were similar to those of the tungstates, but deeper in tint.

The tendency of the precipitates to adhere to the sides of the beaker was a serious source of error at first; particularly after boiling, when it seemed impossible to remove them entirely. If not heated above 70° C. a piece of moist filter will remove the adherent precipitate better than anything; in most cases it removes it perfectly, while a rubber is useless.

The ignitions were all made with free access of air, and were continued for at least two hours. Apparently no reduction of the molybdic acid takes place, as a second ignition after moistening with ammonium nitrate, or with nitric acid, causes no change in the weight.

The solubilities were determined by the Victor Meyer Method.* It will be noticed that with the praseodymium salts the solubility increases with a rise in temperature, the increase being more marked with the tungstate than with the molybdate.

With neodymium tungstate the solubility decreases as the temperature rises, while with the molybdate it increases under the same conditions. Slight though the solubility is, it is sufficiently great to cause decided error in the results when such small quantities are taken as were used in the experiments here recorded.

* *Berichte* 8. 998. 1875.

It was found very difficult at first when analyzing the salts to obtain a constant weight for the oxides, the results being all higher than theory required. The method finally adopted proved very satisfactory. The precipitated oxalate was strongly ignited together with the filter paper, in a covered platinum crucible, for half an hour, cooled, and moistened with saturated solution of oxalic acid, then ignited again in the covered crucible.

The excess of weight in the earlier analyses being greater than was called for by oxidation to the peroxides, Nd_4O_7 and Pr_4O_7 , the following experiments were made to determine how much oxygen would be taken up by the oxides after they had been reduced to the sesquioxides. In the analyses of neodymium molybdate, the theoretical amount required for the quantity taken was 0.0865 gram, the amount obtained was 0.0863 gram. This was heated in a platinum crucible with a Bunsen burner, the flame being applied at the back of the crucible, while the oxide was drawn forward to prevent any action of reducing gases, as far as possible. The cover of the crucible was bent and placed so as to cause a current of air to pass over the oxide.

From time to time the crucible was cooled and weighed. The following table shows the gain in weight observed and the length of time for which the heat had been applied. It is assumed that the weight first taken represents the sesquioxide, and the atomic mass is taken as 140.5.

Time of heating.	Weight.	Gain.	Oxide.
0 hours.	.0863 gramme.	.0000	Nd_2O_3 .
4 "	.0888 "	.0025	Nd_4O_7 .
5 "	.0892 "	.0029	
7½ "	.0906 "	.0043	Nd_2O_4 ?
10½ "	.0937 "	.0074	
16 "	.0958 "	.0095	
22 "	.0997 "	.0134	Nd_2O_6 ?
27½ "	.1035 "	.0172	Nd_2O_7 ?
30½ "	.1036 "	.0173	

The oxide on first heating changed to a light brown, the color of the superoxide prepared by the Welsbach Company; as the heat was continued it grew lighter in color, until, when it had attained its maximum weight, it was almost pure white.

If the flame is placed directly under the oxide, it loses weight and gradually passes into the brown "superoxide," Nd_4O_7 .

A similar experiment with praseodymium sesquioxide, Pr_2O_3 , gave the following results:

Time of heating.	Weight.	Gain.	Oxide.
0 hours.	.0668 gramme.	0	Pr_2O_3 .
4 "	.0706 "	.0038	Pr_2O_4 ?
6 "	.0722 "	.0054	
8 "	.0730 "	.0062	Pr_2O_5 ?
11 "	.0745 "	.0077	
13 "	.0749 "	.0081	

The atomic mass of praseodymium is taken at 143.5. The color of the oxide changed in the same way as that of neodymium, passing rapidly into the black peroxide Pr_4O_7 of Welsbach, then slowly changing to a reddish brown, and gradually becoming quite light in color. Whether it would be possible to increase the weight still more by heating small quantities for a long period of time, can only be determined by experiment; but the indications point to the existence of praseodymium trioxide PrO_3 , as the increase in weight obtained is greater than that required for Pr_2O_5 .

It would appear that the oxide Nd_2O_7 can be formed, improbable as it may seem, and that it is comparatively stable.

If it is really Nd_2O_7 , neodymium is properly classed with manganese in the seventh group. It would be interesting to know if by reduction the monoxide NdO could also be formed.

The results of my work with these rare and interesting earths will now be given as briefly as possible. The

principal variations in the methods used were those relating to time and temperature, as the solutions were quite dilute, and the material too scant to study the effect of using solutions of different degrees of concentration.

Sodium Tungstate and Praseodymium Chloride.

Atomic mass of praseodymium = 143.5.

The solution of sodium tungstate contained 5 grammes in one litre.

Exp. 1. Ten cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and 25 cc. of 95 per cent alcohol were added, followed by 5 cc. of praseodymium chloride solution in the cold. A precipitate formed at once, and the whole was boiled for an hour; it was then filtered, washed with hot water containing 25 per cent of alcohol, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.0579 grm.	0.0586.	—0.0007.

Exp. 2. Ten cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and 25 cc. of alcohol added. The whole was brought to boiling, and 5 cc. of the praseodymium chloride solution added, after which the boiling was continued for an hour. The precipitate was then filtered off, and washed with cold water, containing 20 per cent of alcohol. The filtrate showed a slight opalescence, which was not removed by refiltering.

Wt. obtained.	Calculated.	Difference.
0.0540 grm.	0.0586.	—0.0046.

Exp. 3. Twenty cc. of the sodium tungstate solution were diluted with 75 cc. of distilled water, and 5 cc. of the praseodymium chloride added. The whole was then boiled for

an hour, allowed to cool, and filtered cold, the washing being done with cold water.

Wt. obtained.	Calculated.	Difference.
0.1091 grm.	0.1172.	—0.0081.

Exp. 4. Twenty cc. of sodium tungstate solution were diluted to 100 cc. with distilled water, and 5 cc. of the praseodymium chloride solution added. The whole was allowed to stand for twelve hours, then brought to boiling, filtered hot, and washed with boiling water.

Wt. obtained.	Calculated.	Difference.
0.1136 grm.	0.1172.	—0.0036.

The filtrate was boiled for an hour with 50 cc. of 95 per cent alcohol, but no additional precipitate was obtained.

Exps. 5 and 6. Twenty cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and 5 cc. of the praseodymium chloride solution added, followed by 50 cc. of 95 per cent alcohol. The whole was then boiled, filtered while hot, and washed with hot water containing 33 per cent of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Exp. 5.</i>	0.1200 grm.	0.1172.	0.0028.
" 6.	0.1230 "	0.1172.	0.0058.

Exps. 7, 8 and 9. Thirty cc. of the sodium tungstate solution were diluted to 75 cc. with distilled water, and 6 cc. of the praseodymium chloride added, followed by 25 cc. of 95 per cent alcohol. The whole was heated to 60° C. for half an hour, filtered while hot, and the precipitate washed with hot water containing 25 per cent of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Exp. 7.</i>	0.1733 grm.	0.1758.	—0.0025.
" 8.	0.1730 "	0.1758.	—0.0028.
" 9.	0.1724 "	0.1758.	—0.0034.

The precipitates after ignition showed traces of the blackish-brown praseodymium peroxide Pr_4O_7 . The filtrate was tested with hydrogen sulphide, but gave no reaction for tungsten.

Exps. 10, 11, 12, 13 and 14. Thirty cc. of the sodium tungstate solution were diluted to 75 cc. with distilled water, 6 cc. of the praseodymium chloride solution, and 25 cc. of alcohol added, and the whole heated for two hours at a temperature of 60° C. The precipitate was filtered off while the solution was hot, and was washed with 150 cc. hot water, containing 25 per cent of alcohol.

	Wt. obtained.	Calculated.	Difference
<i>Exp. 10.</i>	0.1715 gm.	0.1758.	—0.0043.
" <i>11.</i>	0.1712 "	0.1758.	—0.0046.
" <i>12.</i>	0.1713 "	0.1758.	—0.0045.
" <i>13.</i>	0.1712 "	0.1758.	—0.0046.
" <i>14.</i>	0.1713 "	0.1758.	—0.0045.

The ignited precipitates appeared to be homogeneous, no traces of Pr_4O_7 showing.

The filtrates were all tested for tungsten with hydrogen sulphide, but no tungsten trisulphide was obtained. This test is not of much value, however, when alcohol is present, as that will prevent the precipitation of tungsten as sulphide to a great extent, so that small quantities will escape detection, unless the alcohol is removed by evaporation before the hydrogen sulphide is used. The precipitation of molybdenum does not seem to be hindered under the same conditions, the hydrogen sulphide bringing down minute traces in a solution containing 33 per cent of alcohol.

As the error is constant, and the condition of precipitation the same for all the numbers of this series of experiments, it is probably due to the solubility of praseodymium tungstate in water containing alcohol.

Analysis of Praseodymium Tungstate.

One-tenth of a gramme of the salt was fused with three grammes of equal parts of sodium carbonate and sulphur.

The fused mass was taken up with water, the gray-green insoluble residue filtered off, and washed with cold water; the filtrate was acidified with hydrochloric acid, the precipitated tungsten trisulphide filtered off on a tared filter, and dried in the air bath at 100° C. until a constant weight was obtained.

When allowance is made for the molybdic acid present in sodium tungstate the amount of sulphide obtained must be lower than that called for by theory for pure praseodymium tungstate. The praseodymium oxide should be slightly higher in amount.

To estimate the oxide the insoluble residue from the fusion was dissolved in hydrochloric acid, precipitated with oxalic acid and ammonium hydrate, and ignited in a covered crucible as already described.

	Wt. obtained.	Calculated.	Theoretical.
Pr_2O_3	0.0334 gm.	0.0331.	0.0325.
WS_3	0.0806 "	0.0808.	0.0814.

These results leave no doubt but that the constitution of this salt is correctly represented by the formula $\text{Pr}_2(\text{WO}_4)_3$.

To determine the solubility of the salt, praseodymium chloride was precipitated by sodium tungstate in aqueous solution, the precipitate with the solution was heated to 60°C . for two hours before filtering, and was washed with hot water until silver nitrate showed no trace of chlorine. The precipitate was dried in the air for a week, and then finely powdered. Portions of the salt were mixed with distilled water at different temperatures, about 80 cc. of water being taken for each portion, and then allowed to stand for two hours, the temperature being kept constant and the liquid frequently stirred. At the end of two hours they were filtered into weighed porcelain crucibles, evaporated to dryness, ignited and weighed.

The results obtained are given below.

Temperature.	Wt. of solution.	$\text{Pr}_2(\text{WO}_4)_3$.	Solubility.
20° C.	39.3817 grms.	0.	0.
20° C.	44.6541 "	0.	0.
75° C.	44.2312 "	.0019.	1:23300.
75° C.	40.1484 "	.0018.	1:22300.

The effect of alcohol on the solubility was not determined.

Sodium Molybdate and Praseodymium Chloride.

The solution of sodium molybdate used contained 8.51 grammes in one litre.

Exps. 1-6. Twenty cc. of the sodium molybdate solution were diluted to 70 cc. with distilled water, then 12 cc. praseodymium chloride solution were added, followed by 25 cc. of alcohol. The whole was heated for two hours at a temperature of 65°C. The precipitate was then filtered off and washed with 150 cc. of hot water containing 25 per cent of alcohol, ignited and weighed.

	Wt. obtained.	Calculated.	Difference.
<i>Exp. 1.</i>	0.2093 grm.	0.2101.	—0.0008.
" 2.	0.2094 "	"	—0.0007.
" 3.	0.2096 "	"	—0.0005.
" 4.	0.2084 "	"	—0.0017.
" 5.	0.2084 "	"	—0.0017.
" 6.	0.2080 "	"	—0.0021.

The precipitates numbered 1, 2 and 3, all showed traces of praseodymium oxide Pr_4O_7 ; the others seemed to be homogeneous.

The filtrates were all tested for molybdenum, with zinc, hydrochloric acid and potassium sulphocyanide, but none was found. Alcohol does not interfere with the delicacy of this test.

The ignited salt was analyzed, the molybdic acid being determined by the Pechard method already described, while the praseodymium oxide was determined in the residue, after the molybdic acid was expelled, by the same method as had been pursued with the tungstate.

	Wt. obtained.	Calculated.
WO_3	0.1135 gm.	0.1127.
Pr_2O_3	0.0874 "	0.0873.

The amount taken for analysis was two-tenths of a gramme, and the results show the correct formula to be $\text{Pr}_2(\text{MoO}_4)_3$ corresponding to that found for the tungstate.

The solubility of praseodymium molybdate was determined with the following results:

Temperature.	Wt. of solution.	$\text{Pr}_2(\text{MoO}_4)_3$.	Solubility.
23° C.	71.4000 grms.	0.0011.	1:65820.
75° C.	69.8000 "	0.0010.	1:69800.

Precipitation of Tungstic Acid with Neodymium Chloride.

Atomic mass of neodymium = 140.5.

The solution of sodium tungstate used contained 5 grammes in one litre.

Exps. 1 and 2. Twenty cc. of the sodium tungstate were diluted to 100 cc. with distilled water and 5 cc. of the neodymium chloride added, followed by 25 cc. of 95 per cent alcohol. The whole was brought to boiling, filtered while hot, and the precipitate washed with hot water containing 25 per cent of alcohol.

The filtrates were opalescent, and repeated filtrations failed to render them clear. The precipitates after ignition appeared to be homogeneous.

	Wt. obtained.	Calculated.	Difference.
<i>Exp. 1.</i>	0.1117 gm.	0.1167.	—0.0050.
" 2.	0.1126 "	0.1167.	—0.0041.

Exps. 3 and 4. Ten cc. of the sodium tungstate solution diluted to 50 cc. with distilled water, and $3\frac{1}{2}$ cc. of neodymium chloride solution added were heated to boiling, filtered while hot and the precipitate washed with hot water.

	Wt. obtained.	Calculated.	Difference.
<i>Exps. 3.</i>	0.0595 gm.	0.0583.	0.0012.
" 4.	0.0573 "	0.0583.	-0.0010.

Exps. 5-16. These experiments were duplicates of 3 and 4, excepting that the solutions were heated to 80°C. instead of to boiling. No alcohol was added, and the precipitates were washed with hot water. The precipitates showed traces of the brown peroxide, Nd_4O_7 .

	Wt. obtained.	Calculated.	Difference.
<i>Exp. 5.</i>	0.0575 gm.	0.0583.	-0.0008.
" 6.	0.0575 "	"	-0.0008.
" 7.	0.0593 "	"	+0.0001.
" 8.	0.0600 "	"	0.0017.
" 9.	0.0585 "	"	0.0002.
" 10.	0.0586 "	"	0.0003.
" 11.	0.0590 "	"	0.0007.
" 12.	0.0585 "	"	0.0002.
" 13.	0.0585 "	"	0.0002.
" 14.	0.0581 "	"	-0.0002.
" 15.	0.0584 "	"	0.0001.
" 16.	0.0597 "	"	0.0014.

Exps. 17-18. Thirty cc. of the sodium tungstate solution were diluted to 70 cc. with distilled water and 6 cc. of the neodymium chloride solution added, followed by 25 cc. of alcohol. The whole was heated to 70°C., filtered while hot, and the precipitate washed with hot water containing 25 per cent of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Exp. 17.</i>	0.1724 gm.	0.1749.	-0.0025.
" 18.	0.1745 "	0.1749.	-0.0004.

No. 18 showed slight traces of the peroxide Nd_4O_7 .

Exps. 19-21. These were prepared like the preceding solutions Nos. 17 and 18, but were heated to 60°C. instead of 70°.

The filtrates showed no trace of molybdenum when tested with zinc, hydrochloric acid and potassium sulphocyanide.

	Wt. obtained.	Calculated.	Difference.
<i>Exp.</i> 19.	0.1731.	0.1749.	—0.0018.
" 20.	0.1727.	0.1749.	—0.0022.
" 21.	0.1728.	0.1749.	—0.0021.

A comparison of these results shows that the precipitation of tungstic acid by neodymium chloride is practically quantitative. Analyses of the salt made in the same manner as for praseodymium tungstate agreed closely with the theoretical requirements as regarded the neodymium oxide. The tungstic acid was invariably too low, and the different results were too discordant, the tungstic acid therefore was determined by difference; the weight of neodymium oxide found was 0.0651 gramme, the amount required by theory being 0.0652 gramme. From this was deduced the formula $\text{Nd}_2(\text{WO}_4)_3$ for the salt, which corresponds to the praseodymium tungstate.

The solubilities, determined as for the praseodymium salts, and under similar conditions were as follows:

Temperature.	Wt. of solution.	$\text{Nd}_2(\text{WO}_4)_3$.	Solubility.
22° C.	42.1032 grms.	0.0008.	1:52630.
65° C.	41.7117 "	0.0007.	1:59580.
98° C.	39.6286 "	0.0006.	1:66040.

Sodium Molybdate and Neodymium Chloride.

The solution of sodium molybdate used contained 5.1080 grammes in one litre.

Exps. 1-5. Twenty cc. of the sodium molybdate solution were diluted to 70 cc. with distilled water, 7 cc. of the neodymium chloride solution were added, followed by 25 cc. of 95 per cent alcohol. The whole was then heated to

65°C. for two hours, filtered hot and the precipitate washed with 150 cc. of hot water containing 25 per cent of alcohol.

The ignited precipitates showed no trace of the brown oxide Nd_2O_3 , and the filtrates when tested gave no reaction for molybdenum.

	Wt. obtained.	Calculated.	Difference.
<i>Exp. 1.</i>	0.1260 grm.	0.1256.	0.0004.
" 2.	0.1259 "	"	0.0003.
" 3.	0.1260 "	"	0.0004.
" 4.	0.1259 "	"	0.0003.
" 5.	0.1258 "	"	0.0002.

An analysis of two-tenths of a gramme of the salt made in the same way as the analysis of praseodymium molybdate gave the following results :

	Wt. obtained.	Calculated.	Difference.
Nd_2O_3	0.0863 grm.	0.0865.	—0.0002.
MoO_3	0.1134 "	0.1135.	—0.0001.

From these results the formula $\text{Nd}_2(\text{MoO}_4)_3$ is deduced for neodymium molybdate.

The solubility determinations gave the following results :

Temperature.	Wt. of solution.	$\text{Nd}_2(\text{MoO}_4)_3$.	Solubility.
28° C.	69.9311 grms.	0.0013.	1:53790.
75° C.	71.4279 "	0.0022.	1:32466.

A comparison of the results obtained shows that the precipitation of both tungstic and molybdic acids by neodymium salts is quantitative.

Precipitation of Tungstic and Molybdic Acids by Lanthanum Chloride.

Atomic mass of lanthanum = 138.2.

The lanthanum chloride used was prepared in this laboratory from lanthanite, and appeared to be quite pure.

The precipitates obtained were similar in character to those obtained from the neodymium and praseodymium salts.

The tungstate before ignition was of a delicate blue, almost white, and after ignition the color deepened slightly. The color of the molybdate was almost the same as that of the tungstate.

Sodium Tungstate and Lanthanum Chloride.

The solution of sodium tungstate contained 5 grammes in a litre.

Exps. 1 and 2. Twenty cc. of sodium tungstate solution were diluted to 70 cc. with distilled water, and 7 cc. of lanthanum chloride solution added, followed by 25 cc. of alcohol. The whole was heated for two hours at a temperature of 60°C., after which the precipitate was filtered off and washed with 150 cc. of hot water containing 25 per cent of alcohol. The filtrate was clear and gave no reaction for tungsten with hydrogen sulphide. The ignited precipitates appeared to be homogeneous.

	Wt. obtained.	Calculated.	Difference.
<i>Exp. 1.</i>	0.1143 gm.	0.1160.	—0.0017.
" 2.	0.1143 "	"	—0.0017.

Analysis of Lanthanum Tungstate.

The first analysis was made by fusing with sodium carbonate and sulphur, then taking up in water, and filtering off the sodium sulpho-tungstate formed, from the

insoluble lanthanum oxide; then decomposing the filtrate with hydrochloric acid and estimating the tungsten from the tungsten trisulphide found.

The results obtained were very satisfactory so far as the lanthanum oxide was concerned, but no good results were obtained for the tungstic acid.

The amount of the salt taken for analysis was one-tenth of a gramme.

	Wt. obtained.	Calculated.
La_2O_3 .	0.0326 gm.	0.0321.
WS_3 .	0.0606 "	0.0822.

The same difficulty was encountered here that was met with in the analysis of neodymium tungstate, and the cause was not apparent. A second analysis by a different method was made, the same amount of material being taken. The lanthanum tungstate was decomposed with aqua regia, evaporated to dryness with hydrochloric acid three times, and the separated tungstic trioxide filtered off and dissolved in ammonium hydrate; the filtrate was rendered ammoniacal, the solution of the tungstic acid added to it, and hydrogen sulphide passed through it until the liquid was deep yellow in color. The liquid was acidified with hydrochloric acid, and before neutralization was complete the color changed to a bright green, becoming red when completely acidified. On rendering it ammoniacal again, the green color reappeared.

Hydrogen sulphide was passed through the solution again for an hour, hydrochloric acid added and the solution warmed; it gradually became colorless, and a light brown precipitate of tungsten trisulphide settled down.

This was treated in the usual manner and dried at 100° to constant weight.

	Wt. obtained.	Calculated.
WS_3 .	0.0640 gm.	0.0822.

The filtrate was boiled until all the hydrogen sulphide was expelled; a few drops of nitric acid added, and then ammonium hydrate; the precipitate of lanthanum hydrate was evidently not pure, being yellow in color instead of white; it was filtered off, ignited, dissolved in aqua regia, evaporated to dryness, taken up with a little hydrochloric acid, followed by ammonia and the treatment with hydrogen sulphide repeated. The yellow ammoniacal solution passed through the same color changes as before, when acidified. On heating, a dark red-brown precipitate formed, which was filtered off, and washed with dilute hydrochloric acid, and then with alcohol. A great part of the precipitate dissolved in the alcohol to a dark red solution, the precipitate left on the filter paper turning brown. This precipitate was ignited in a weighed porcelain crucible and evaporated with concentrated nitric acid until a constant weight was obtained. It had the appearance of tungstic acid.

Wt. obtained = 0.0073 grm.

The alcoholic filtrate was evaporated to dryness in a weighed porcelain crucible, and treated repeatedly with fuming nitric acid to oxidize any sulphur that might be present to sulphuric acid, which was removed by repeated evaporation with ammonium hydrate. The substance remaining in the porcelain crucible had the appearance of molybdic acid. It was pale yellow in color, was readily soluble in ammonium hydrate, and also dissolved in aqua regia to a bright yellow solution, separating out as a bright yellow powder on concentrating the solution. The yellow powder when ignited turned brown, but regained its color on cooling, finally, however, becoming lemon yellow. When moistened with hydrochloric acid and heated, no blue color appeared. A faint orange red solution was obtained by treatment with zinc, hydrochloric acid and potassium sulpho

cyanide. Heated on platinum foil with con. sulphuric acid no blue color was produced. The phosphorus bead was colorless, even after treating with tin on charcoal.

The weight obtained was 0.0076 gramme. The second analysis gives the following results:

	Wt. obtained.	Calculated.
La_2O_3 .	0.0326.	0.0321.
WO_3 .	.0613.	.0679.
2.	.0076.	

This corresponds to the formula $\text{La}_2(\text{WO}_4)_3$ for lanthanum tungstate. The same salt was prepared by W. French Smith⁵ by the precipitation of sodium tungstate with lanthanum salts.

The solubility of lanthanum tungstate in water was determined by the Victor Meyer method already referred to, the salt being prepared in the same way as the praseodymium tungstate.

Temperature.	Wt. of solution.	$\text{La}_2(\text{WO}_4)_3$.	Solubility.
27° C.	60.5580 grms.	.0007.	1:86510.
65° C.	42.4678 "	.0010.	1:42467.

Sodium Molybdate and Lanthanum Chloride.

The solution of sodium molybdate used contained 8.51 grammes in one litre.

Exps. 1-3. Twenty cc. sodium molybdate solution were diluted to 70 cc. with distilled water, 7 cc. of lanthanum chloride solution added, followed by 25 cc. of 95 per cent alcohol.

⁵ "Ueber Didymium and Lanthanum." Inaugural Dissertation by W. French Smith. Göttingen, 1875.

The precipitate, at first gelatinous, gradually became granular, and was filtered off, washed with 150 cc. hot water containing 25 per cent of alcohol, ignited and weighed.

	Wt. obtained.	Calculated.	Difference.
<i>Exp. 1.</i>	0.2063 grm.	0.2083.	—0.0020.
" 2.	0.2061 "	0.2083.	—0.0022.
" 3.	0.2053 "	0.2083.	—0.0020.

The filtrates were clear and gave no reaction for molybdenum when treated with potassium sulphocyanide in the presence of zinc and hydrochloric acid.

The solubility of the salt obtained was determined under the following conditions :

Temperature.	Wt. of solution.	$\text{La}_2(\text{MoO}_4)_3$.	Solubility.
25° C.	72.5500 grms.	.0013.	1:55800.
85° C.	69.3474 "	.0023.	1:30150.

* Analysis of Lanthanum Molybdate.

The analysis was made in the same manner as with the other molybdates, the salt being decomposed in a current of dry hydrogen chloride gas. The molybdic acid was driven off very readily at first, but toward the close of the operation the full heat of the Bunsen burner was required. Two-tenths of a gramme of the salt were taken for analysis, and results were as follows :

	Wt. obtained.	Calculated.
La_2O_3	0.0853.	0.0856.
MoO_3	0.1145.	0.1144.

From these results the formula $\text{La}_2(\text{MoO}_4)_3$ may be calculated for lanthanum molybdate.

Tests were now made with thorium chloride, potassium zirconium fluoride and zirconium fluoride.

With thorium chloride no definite results could be obtained from either sodium molybdate or sodium tungstate; precipitates were formed with both salts even in

quite dilute solutions, but they were slight in quantity, and ran through the filter in spite of every attempt to prevent it, whether filtered hot or cold. Neither alcohol nor ammonium salts made any difference in the behavior.

With the potassium zirconium fluoride no precipitate was obtained with either the tungstate of sodium or the molybdate.

With zirconium fluoride no results were obtained, the solutions remaining clear after standing several days.

Beyond these qualitative tests no work was done with the thorium or zirconium salts in connection with tungsten and molybdenum.

Summary.

1. The tungstates and molybdates are precipitated quantitatively by nearly all the rare earths.

2. A separation of tungstic and molybdic acids is not possible through their combinations with the rare earths.

3. The non-precipitation of molybdic acid by uranyl solutions when tungstates are absent, and the almost complete precipitation of both when tungstic acid is also present is further evidence of the fact that we can scarcely hope to effect this separation by the method of precipitation.

4. The molybdates and tungstates of neodymium and praseodymium are new, and their constitution is correctly represented by the formulæ $\text{Nd}_2(\text{MoO}_4)_3$, $\text{Nd}_2(\text{WO}_4)_3$ and $\text{Pr}_2(\text{MoO}_4)_3$, $\text{Pr}_2(\text{WO}_4)_3$.

5. The solubility determinations indicate that tungstates and molybdates of the rare earths must be classed among the more difficultly soluble compounds.

6. Further research is required upon the methods to be followed in the separation of tungstic and molybdic acids from the oxides of the rare earths.

